(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 559 096 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **93103086.0**

(22) Date of filing: **26.02.93**

(51) Int. Cl.5: **C22F 1/18**, G01N 21/21, G01N 27/72, //G21C3/07

(30) Priority: **06.03.92 US 847513**

(43) Date of publication of application: **08.09.93 Bulletin 93/36**

(84) Designated Contracting States: **BE CH DE ES FR GB LI SE**

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(54) Zirlo alloy and method for fabrication.

(57) A Zirlo alloy formed by beta quenching, hot deforming, recrystallize annealing and then cold deforming said alloy a plurality of times with recrystallize anneal steps performed between the cold deforming steps followed by stress relief annealing. The fabricating method can include a late stage beta quench step in place of one of the recrystallize anneal steps. The recrystallization anneals take place at 649 to 760 °C.

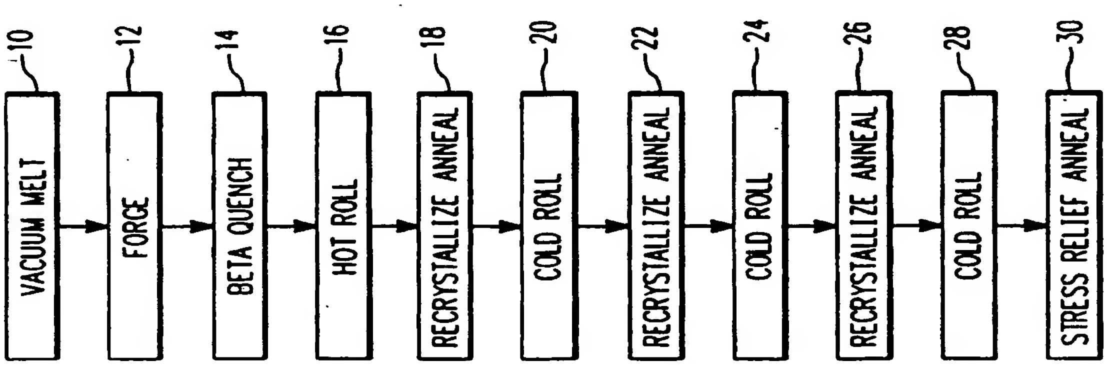

FIG. 1

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The present invention relates to a Zirlo alloy and to a method for fabricating a Zirloy alloy in tubes or strips. Zirlo is used in the elevated temperature aqueous environment of a rector of a nuclear plant and is an alloy of primarily zirconium containing nominally by weight 1 percent niobium, 1 percent tin and 0.1 percent iron. Generally, Zirlo comprises 0.5 to 2.0 weight percent niobium, 0.7 to 1.5 weight percent tin and 0.07 to 0.28 of at least one of iron, nickel and chromium and up to 200 ppm carbon. The balance of the alloy comprises essentially zirconium.

Among the objectives of fabrication methods for Zirlo are obtaining good corrosion resistance with acceptable texture. The relationship between pilger reduction formability and texture parameters are presented below by first describing the formability parameter and then showing the applicability of the formability parameter to pilger reduction.

The formability parameter describes the small and large strain behavior of anisotropic materials such as Zirlo. W. A. Backofen, Deformation Processing, Addison-Wesley Publishing Company, 1972, pp. 85-85, defined the formability parameter B to describe the distortion or anisotropy of the yield locus. Backofen defined the formability parameter as:

$$B = \sigma_I / 2\sigma_{IV}$$

where σ_I is the maximum stress in quadrant I and σ_{IV} represents the shear stress in quadrant IV of the yield locus. The B parameter is important because the higher the B value, the better the material formability. Although the yield behavior is associated with small strains, the formability parameter also describes high strain metalworking operations. For deep cup drawing, the drawing limit is given by the limiting drawing ration, LDR

$$\ln(LDR) = \sigma_w / \sigma_f$$

where σ is the stress and the subscripts w and f denote the cup wall and flange, respectively. W.F. Hosford and R.M. Caddell, Metal Forming Mechanics and Metallurgy, Prentice-Hall, 1983, pp. 277-279, have shown for deep cup drawing that the formability parameter is related to the LDR according to the equation

$$B = \ln(LDR)$$

Hence, the formability parameter describes deep cup drawing.

Pilger reduction and deep cup drawing are considered to be related processes based on the similarity between the stresses and strains developed during pilgering and deep cup drawing. Pilgering is a direct compression metalworking operation. A force is applied to the tube-shell surface by the die and metal flows at right angles to the applied force. In the case of deep cup drawing, the applied force is tensile, but large compressive forces are developed by the reaction of the workpiece and the die. More specifically, as the metal is inwardly drawn, the outer circumference continually decreases. This means that in the flange region the workpiece is subject to compressive hoop strain and stress. Hence both pilgering and deep cup drawing may be considered to be similar metalworking operations because they both involve large compressive strain and stress.

The texture of anisotropic tubes is characterized by the transverse contractile strain ratios. The transverse contractile strain ratios of an anisotropic tube define the resistance to wall thinning. The transverse contractile strain ratios are:

$$R = \Delta e_\theta / \Delta e_r \text{ for } \sigma_\theta = \sigma_r = 0$$
$$P = \Delta e_z / \Delta e_r \text{ for } \sigma_z = \sigma_r = 0$$

where θ, z and r are the hoop, axial and radial directions. K. L. Murty, "Application of Crystallographic Textures of Zirconium Alloys in the Nuclear Industry", Zirconium in the Nuclear Industry: Eight International Symposium, ASTM STP 1023, American Society for Testing and Materials, Philadelphia, 1989, pp. 570-595, has developed the relationship between the formability parameter and the contractile strain ratios R and P. The relationship is

$$B = [\{(R+1)\,(R+4RP+P)\}/\{4R(R+P+1)\}]^{0.5}$$

A pilger reduction operation is considered successful when a defect free tube is produced. The production of a defect free tubeshell depends on whether the hoop and/or axial stress remains below the

tensile strength of the metal near the ID surface. When the hoop and/or axial stress exceeds the tensile strength of the metal near the tubeshell ID surface, the tubeshell develops small tears or microfissures. Presumably, an increase in the formability parameter is associated with a decrease in the tendency for microfissure development.

In the course of the following detailed description of the present invention, reference will be made to the following Figures in which:

Figure 1 shows a sequence of steps for forming Zirlo strip.

Figure 2 shows a modified sequence of steps for forming Zirlo strip.

Figures 3, 4 and 5 show photomicrographs of Zirlo fabricated at various temperatures.

In accordance with this invention, improved Zirlo formability may be obtained by fabricating Zirlo employing higher recrystallization temperatures than have been employed heretofore.

Zirlo strip material was processed according to the schematic process outline presented in Figure 1, discussed in more detail below. The recrystallization anneals were performed at temperatures of 593°C (1100°F), 677°C (1250°F) and 732°C (1350°F), respectively. Longitudinal and transverse direction uniaxial tensile samples were cut from the strip and tested to measure the transverse contractile strain ratio parameters R and P. In a uniaxial strip sample, the transverse contractile strain ratios are

$R = \Delta e_t/\Delta e_n$ for $\sigma_n = \sigma_t = 0$

$P = \Delta e_r/\Delta e_n$ for $\sigma_n = \sigma_r = 0$

where r, n and t denote the rolling, normal and transverse directions of the strip, respectively.

We have found that use of a recrystallization anneal temperature higher than those employed heretofore in the process scheme of Figure 1 increases formability or fabricability. Table 1 shows for the uniaxial strip samples that a recrystallization anneal temperature within the range of this invention increases the formability parameter B.

TABLE 1

Uniaxial Strip Sample Transverse Contractile Strain Ratio Data and Calculated Formability Parameters			
Recrystallization Anneal Temperature (°C)	R	P	B
593 (1100°F)	2.6	2.7	1.4
677 (1250°F)	5.3	5.4	1.8
732 (1350°F)	3.4	5.0	1.6

Similar results have been observed during tube fabrication.

Table 2 shows that the percentage of tubes accepted (tubes with flaws less than the ultrasonic defect standard) increase with increasing intermediate recrystallization temperature.

TABLE 2

Tube Ultrasonic Flaw Acceptance Data	
Intermediate Recrystallization Anneal Temperature (°C)	Acceptance (%)
593 (1100°F)	93
677 (1250°F)	98

Therefore, an increase in formability decreases defect development during tube reduction.

The observed increase in the formability parameter with intermediate anneal temperature may be due to microstructural changes as well as texture changes. The photo-micrographs of Figures 3, 4 and 5 in the 500X magnification show the microstructure for intermediate anneal temperatures of 593, 677 and 732°C (1100, 1250 and 1350°F), respectively. At 593°C (1100°F), the second phase is uniformly distributed (see Figure 3). However, at 677°C (1250°F), the precipitate size increases with large amounts located at grain boundaries (see Figure 4). Figure 5 shows that at 732°C (1350°F), the second phase precipitate size

increased and almost all of the second phase is located at the grain boundaries. The coarse second phase particle distribution associated with intermediate anneal temperatures of 677 °C (1250 °F) and 732 °C (1350 °F) could exhibit reduced in reactor corrosion resistance. A fine second phase particle distribution may be obtained by performing a late stage beta anneal and water quench after processing the materials with intermediate anneal temperatures above 593 °C (1100 °F). As shown in Table 3, the late stage beta quench will also slightly improve corrosion resistance.

TABLE 3

Corrosion Improvement Due to Beta-Quenching The Tubeshells During Tube Reduction Two Steps Prior to Final Size		
Beta-Quench	Intermediate Anneal Temperature (°C)	371 °C (750 °F) Steam Corrosion Rate (mg/dm²-d)
No	593 (1100 °F)	1.03
Yes	593 (1100 °F)	0.92
No	632 (1170 °F)	1.01
Yes	632 (1170 °F)	0.90

Out-of-reactor autoclave tests suggest similar corrosion behavior for material processed with intermediate anneal temperatures between 593 °C (1100 °F) and 732 °C (1350 °F). Table 4 shows that the corrosion rates for 371 °C (750 °F) and 520 °C (968 °F) steam are similar.

TABLE 4

Corrosion Rates			
Corrosion Test	Test Time (d)	Intermediate Anneal Temperature (°C)	Corrosion Rate mg/dm²-d
371 °C steam	252	593 °C (1100 °F)	2.03
		677 °C (1250 °F)	1.74
		732 °C (1350 °F)	1.60
520 °C steam	15	593 °C (1100 °F)	39.5
		677 °C (1250 °F)	37.4
		732 °C (1350 °F)	38.3

As shown in Table 4, the material processed with intermediate anneal temperatures of 677 °C (1250 °F) and 732 °C (1350 °F) exhibited slightly lower 371 °C (750 °F) and 520 °C (968 °F) steam corrosion rates than material processed at 593 °C (1100 °F).

A sequence of steps for working a plate of Zirlo metal is shown in Figure 1 where 10 indicates vacuum melting of a Zirlo ingot followed by forging at step 12 to produce a billet and beta quenching said billet at step 14. Beta quench step 14 occurs at a temperature of about 1093 °C (2000 °F) and accomplishes an improved dispersion of alloying metals in the zirconium. Beta quench step 14 is followed by hot deforming or roll step 16 which occurs at a temperature of about 571 °C (1060 °F) and accomplishes about a 70 percent reduction which in turn is followed by recrystallize anneal step 18 which occurs at a temperature of about 593 °C (1100 °F). Then follows a plurality of recrystallize anneal cold roll combination steps 18 and 20, 22 and 24 and 26 and 28. Recrystallize anneal steps 18, 22 and 26 are performed at a temperature of 649 to 760 °C (1200 to 1400 °F) generally, and 666 to 688 °C (1230 to 1270 °F), preferably. The cold roll steps 20, 24 and 28 accomplish about a 30% reduction. Although two such combination cold deform or roll and recrystallize anneal steps are shown, additional such combination steps can be employed. Finally, the plate is stress relief annealed at step 30 at a temperature of about 465.5 °C (870 °F).

A more preferred sequence of steps for working a plate of Zirlo metal is shown in Figure 2 where 32 indicates vacuum melting of Zirlo ingot followed by forging step 34 and beta quench step 36. Beta quench step 36 of a billet of the alloy occurs at a temperature of about 1093.3 °C (2000 °F), and accomplishes an improved dispersion of alloying metals in the zirconium. Beta quench step 36 is followed by hot roll step 38 which occurs at a temperature of about 571 °C (1060 °F) and which accomplishes about a 70 percent reduction. Then follows two recrystallization anneal and cold work steps 40 and 43, and 44 and 46.

Recrystallize anneal steps 40 and 44 are performed at a temperature of 649 to 760 °C (1200 to 1400 °F), and preferably at a temperature of 666 to 688 °C (1230 to 1270 °F). The cold roll steps 42 and 46 accomplish about a 30% reduction. Then follows late stage beta quench step 48 which occurs at a higher temperature of about 1093.3 °C (2000 °F). The operation is concluded by cold roll step 50 which accomplishes about a 30% reduction and finally by stress relief anneal step 52 which occurs at about 465.5 °C (870 °F).

IDENTIFICATION OF REFERENCE NUMERALS USED IN THE DRAWINGS		
LEGEND	REF. NO.	FIGURE
VACUUM MELT	10	1
FORCE	12	1
BETA QUENCH	14	1
HOT ROLL	16	1
RECRYSTALLIZE ANNEAL	18	1
COLD ROLL	20	1
RECRYSTALLIZE ANNEAL	22	1
COLD ROLL	24	1
RECRYSTALLIZE ANNEAL	26	1
COLD ROLL	28	1
STRESS RELIEF ANNEAL	30	1
VACUUM MELT	32	2
FORGE	34	2
BETA QUENCH	36	2
HOT ROLL	38	2
RECRYSTALLIZE ANNEAL	40	2
COLD ROLL	42	2
RECRYSTALLIZE ANNEAL	44	2
COLD ROLL	46	2
LATE STAGE BETA QUENCH	48	2
COLD ROLL	50	2
STRESS RELIEF ANNEAL	52	2

Claims

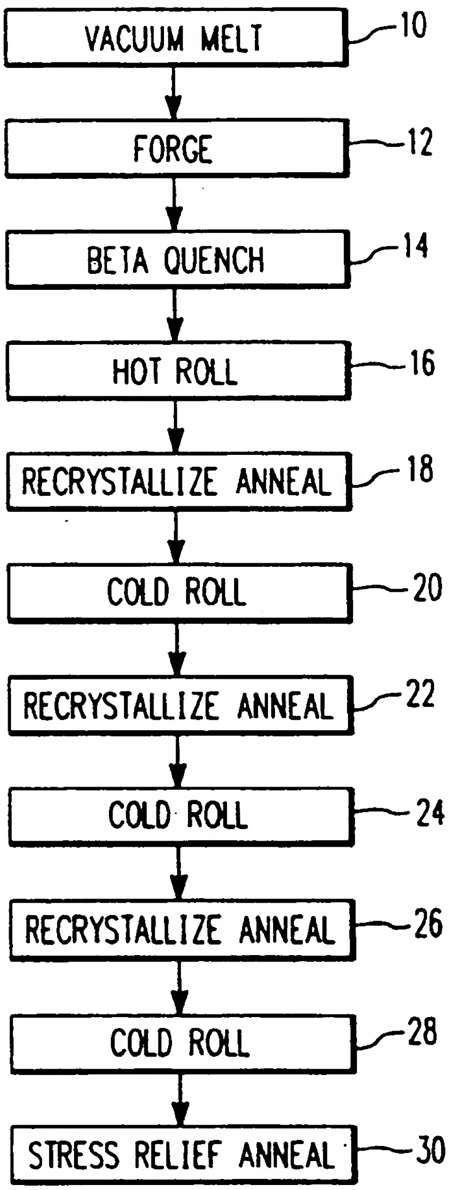
1. A zirconium alloy for use in the elevated temperature aqueous environment of a reactor of a nuclear plant, characterized by:
   0.5 to 2.0 weight percent niobium,
   0.7 to 1.5 weight percent tin,
   0.07 to 0.28 weight percent of at least one of iron,
   nickel and chromium, up to 200 ppm carbon,
   and the balance of said alloy consisting essentially of zirconium,
   said article produced by subjecting the material to a plurality of recrystallization anneal and cold work combination steps, the recrystallization anneal steps being performed at a temperature of 649 to 760 °C (1200 to 1400 °F).

2. The article of manufacture of claim 1 wherein said recrystallization anneal steps are performed at a temperature of 666 to 688 °C (1230 to 1270 °F).

3. A process for fabricating a zirconium alloy characterized by
   0.5 to 2.0 weight percent niobium,
   0.7 to 1.5 weight percent tin,
   0.07 to 0.28 weight percent of at least one member of the group comprising iron, nickel and chromium, up to 200 ppm carbon,
   and the balance of said alloy consisting essentially of zirconium, said process including subjecting the material to a plurality of recrystallization anneal and cold work combination steps followed by a late

stage beta quench, the recrystallization anneal steps being performed at a temperature of 649 to 760 °C (1200 to 1400 °F).

4. The process of claim 1 wherein said recrystallization anneal steps are performed at a temperature of 666 to 688 °C (1230 to 1270 °F).


VACUUM MELT
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FORGE
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BETA QUENCH
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HOT ROLL
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RECRYSTALLIZE ANNEAL
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COLD ROLL
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RECRYSTALLIZE ANNEAL
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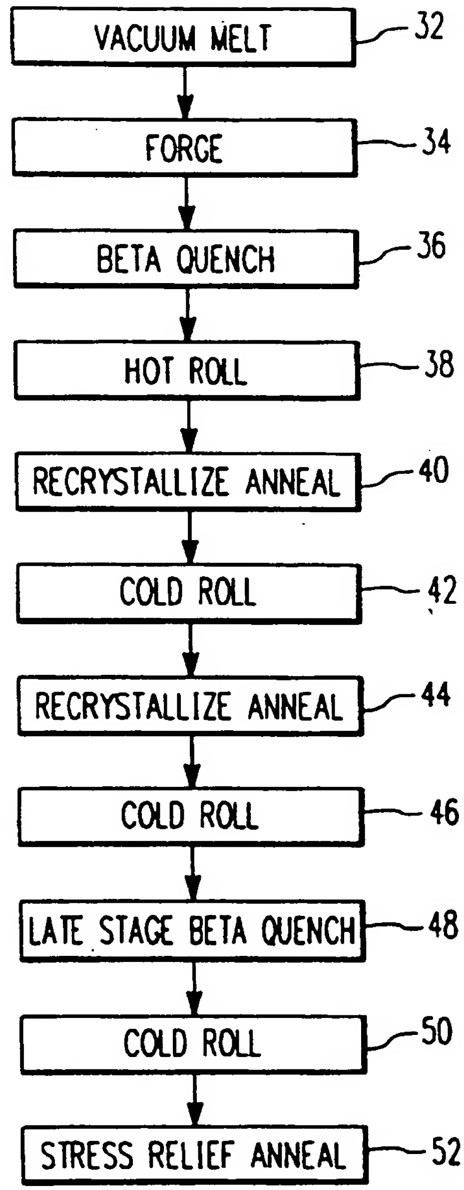
COLD ROLL
24
RECRYSTALLIZE ANNEAL
26
COLD ROLL
28
STRESS RELIEF ANNEAL
30

FIG. 1


VACUUM MELT
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FORGE
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BETA QUENCH
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HOT ROLL
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RECRYSTALLIZE ANNEAL
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COLD ROLL
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RECRYSTALLIZE ANNEAL
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COLD ROLL
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LATE STAGE BETA QUENCH
48
COLD ROLL
50
STRESS RELIEF ANNEAL
52

FIG. 2

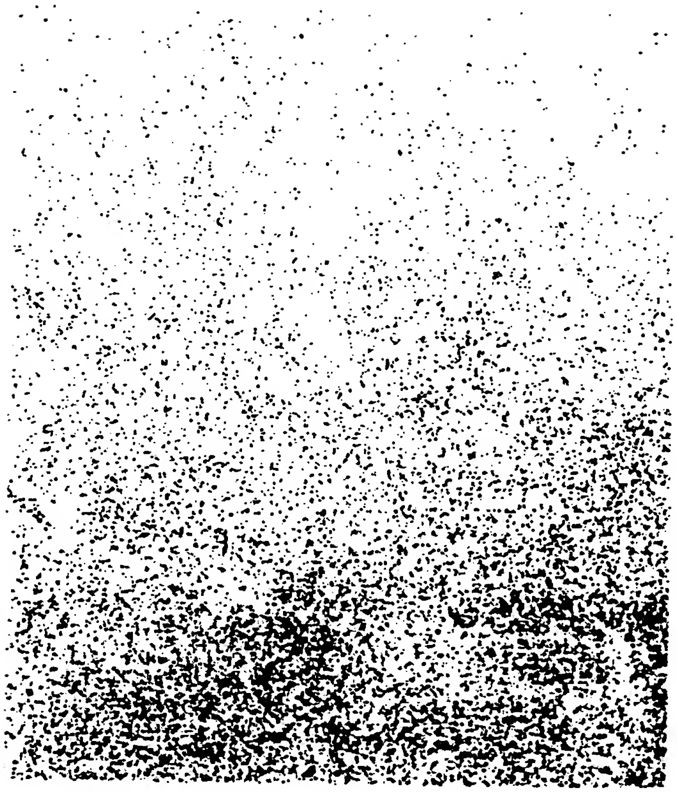

FIG. 3

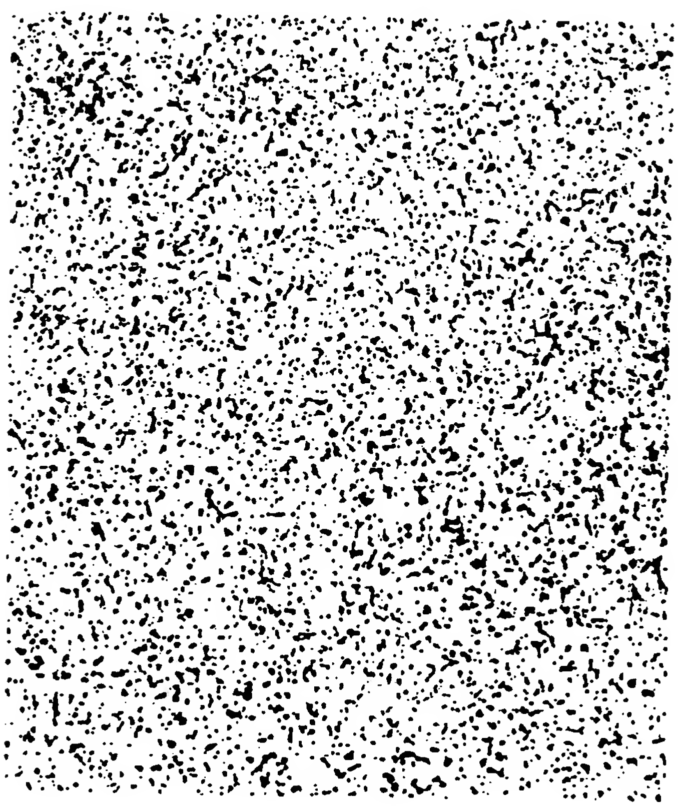

FIG. 4

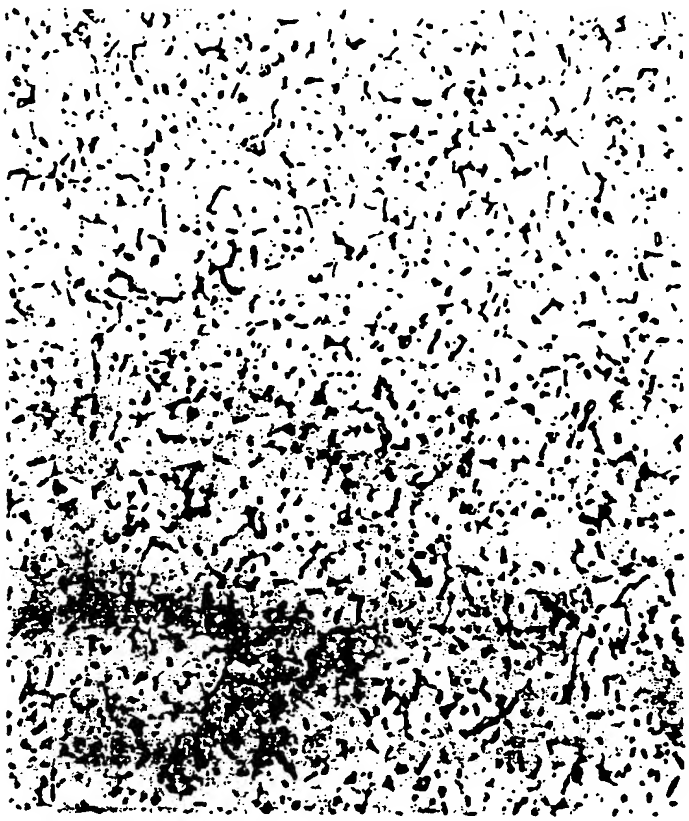

FIG. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 3086

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 415 134 (WESTINGHOUSE ELECTRIC CORPORATION) * claim 8; figure 1 *	1-4	C22F1/18 //G21C3/07
A	FR-A-2 664 907 (CEZUS) * claims 1-6 *	1-4	
A	EP-A-0 098 996 (HITACHI LTD) * page 14, line 8 - line 10; figures 5,6 *	1-4	
A	EP-A-0 196 286 (SANTRADE LTD) * claim 1 *	1-4	
A	EP-A-0 246 986 (CEZUS) * claim 1 *	1-4	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 028 (C-471)27 January 1988 & JP-A-62 180 047 (HITACHI LTD) 7 August 1987 * abstract *	1-4	
A	EP-A-0 198 570 (WESTINGHOUSE ELECTRIC CORPORATION)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 JULY 1993	GREGG N.R.

CATEGORY OF CITED DOCUMENTS

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